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A Calorimetric Determination of the Enthalpy of Ionization of Water and the Enthalpy of Protonation of THAM at 5, 20, 25, 35, and 50°C

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The enthalpy of ionization of water and the enthalpy of protonation of THAM have been measured at five different temperatures *viz.* 5, 20, 25, 35, and 50°C. The standard enthalpy changes for the two reactions at 25°C were determined as 55.84 ± 0.05 kJ and -47.44 ± 0.05 kJ, respectively, in good agreement with the results obtained by other investigators. The found change in heat capacity, $\Delta C_{P,W}^{\infty}$, for the ionization of water agrees with the values of Ackermann obtained by heat capacity measurements. The $\Delta C_{P,A}$ values for the protonation of THAM do not agree well with the results of Bates *et al.* and Datta *et al.*, obtained by emf methods. The values of the corresponding heats of ionization are, however, in better agreement. All calorimetric measurements have been made by using a calorimeter specially designed for a titration technique. The precision of the calorimeter is 0.05–0.15 % for heat changes of about 10 J. The accuracy, as determined by a series of standard reactions at 25°C, is within 0.1–0.2 %.

The temperature dependence of the free energy, enthalpy, and entropy changes for reactions in water solution are of considerable interest both from a practical and a theoretical point of view. The most direct way of obtaining this information is a calorimetric determination of the enthalpy changes at various temperatures and an accurate free energy determination at one reference temperature, say 25°C. In this communication we will describe experimental determinations of the enthalpy changes for two thermochemical standard reactions *viz.* the heat of ionization of water and the heat of protonation of tris(hydroxymethyl)aminomethane, THAM, at the temperatures 5, 20, 25, 35, and 50°C. For this purpose we have designed a reaction calorimeter suitable for titrations in the temperature range 0–60°C.

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DESCRIPTION OF THE CALORIMETRIC SYSTEM

The calorimeter and the temperature recording devices are modifications of systems previously described.[1–3] The calorimeter is of the isothermal jacket type and has a heat exchange device by which a quantity of liquid can be added to the calorimeter from an external piston burette under full temperature control. A more detailed description of the various parts of the system is given below.

The calorimeter. The main features of the calorimeter are shown in Fig. 1. The calorimeter consists of an outer chromium plated brass can (1) with a lid and an inner reaction vessel (2) made of gold. The lids of the two vessels are permanently joined by means of

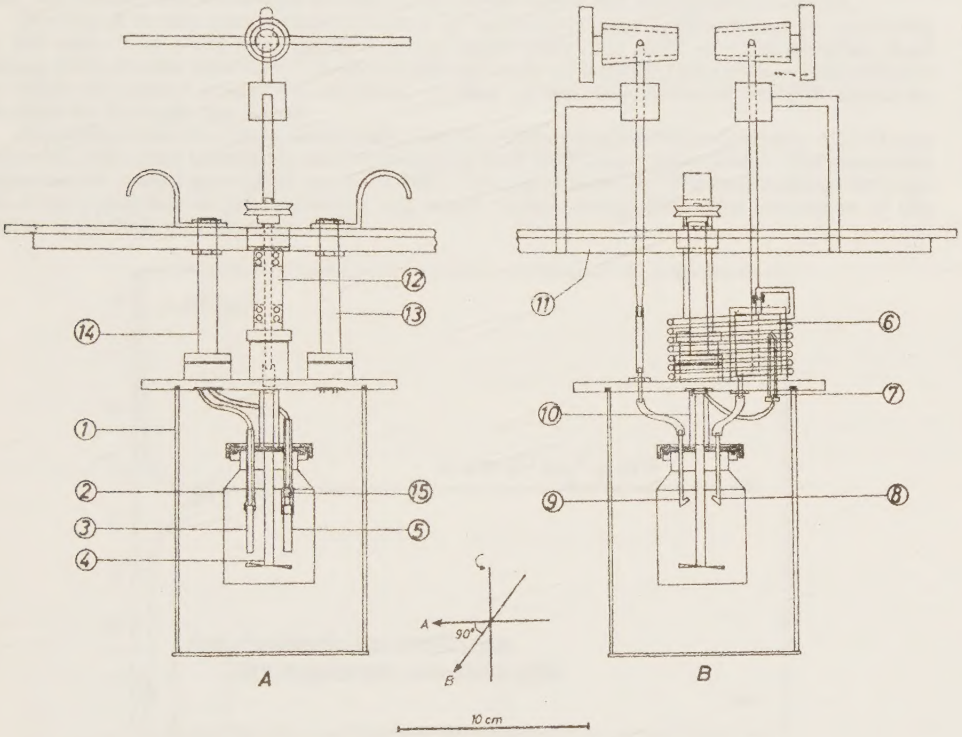

Fig. 1. Calorimeter vessel with jacket as seen from two different directions. For clarity some of the details are only given in one of the figures. The various details are described on pp. 1068 and 1069.

the perspex tube (10), through which the stirrer shaft passes. The outer vessel is fastened to the perspex cover (11) of the thermostat bath *via* three brass chimneys (12–14). These accommodate the stirrer shaft and the electric leads between the inner vessel and the outside. O-ring gaskets give leak-proof seals between the lids and the vessels. Two teflon tubes with gold thimbles (3 and 5), and two 1.50 mm gold tubes (8 and 9) with bent tips are fastened to the inner lid. One tube (5) contains the heater and the other (3)

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the thermistor. Solution is added to or removed from the inner vessel through the tubes (8) and (9) by means of external piston burettes. The tips of the thin gold tubes are bent in order to minimize mixing of the solution in the tubes with that in the calorimeter.

The heat-exchanger (6) consists of two parts. The first part is a chromium plated brass tube into which a brass cylinder with a cut groove fits. The groove accomodates a spiral of gold tubing. The second part is an outer spiral of 2.5 mm glass tubing used to pre-equilibrate the titrant before it passes into the gold spiral. The total volumes of the two spirals are 0.943 cm^3 and 2.806 cm^3, respectively.

The temperature of the heat-exchanger is measured by the thermistor (7) inserted into the brass cylinder. The temperature fluctuations of the thermistor were within 5×10^{-6}°C for a period of 30 min and are so small because the large mass of the outer vessel levels out the larger temperature variations in the thermostat bath. The good thermal contact between the outer casing and the liquid in the heat exchanger means that the titrant can be added to the inner vessel under full temperature control.

The liquid in the inner vessel is stirred by means of the propeller stirrer (4) operating at 750 rpm. The rotor axis consists in its upper part of a shaft of thin stainless steel tubing with double bearings. The lower part is made of a teflon tube with a gold thimble to which the stirrer blades are soldered. Cooling of the calorimeter is brought about by blowing air through the stirrer.

All calibrations are made electrically and the calibration resistance consists of 0.15 mm laquered, silk-spun manganin wire soldered to four 0.50 mm copper leads. The manganin resistance is wound as a spiral on the inside of the gold thimble. Thermal leakage through the teflon chimney is prevented by the small copper block (15). The resistance of the heater is 20.102_7 abs. ohms at 23°C.

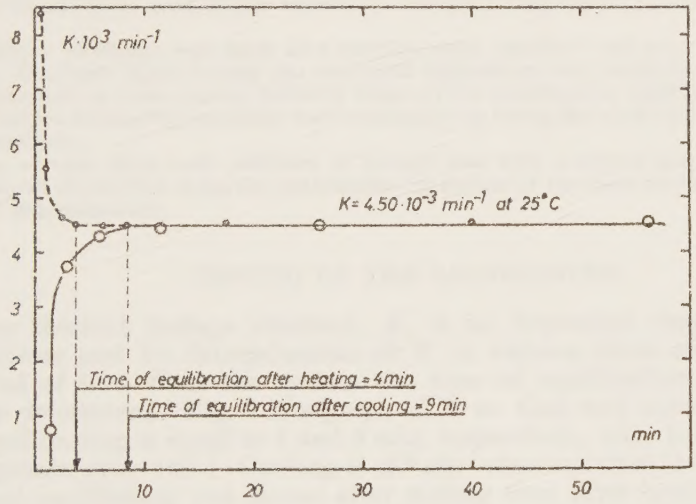

Fig. 2. Plots of the thermal heat leakage constant K *vs.* time, used for determination of the time of equilibration of the calorimeter. The full-drawn curve is obtained after cooling the system approximately 100 J. The dashed curve is obatined after adding the same amount of heat to the system.

Thermostat baths. The thermostat bath used was of type LKB 7603 A and it was cooled by means of water from a second thermostat operated at a temperature 0.8°C below that of the first. Evaporation from the surface of the thermostat bath caused temperature fluctuations larger than 10^{-3}°C when the bath was operated above room

temperature, the perspex cover of the thermostat acting as a cold wall. The temperature fluctuations were decreased to within 5×10^{-4}°C by covering the top of the thermostat with a perspex hood, through which thermostatted air was circulated.

All measurements were made in a thermostatted room at 25.0 ± 0.3°C.

Temperature measurements. The temperature was measured by using a thermistor, VECO T32A47, with a resistance of 2000 Ω at 25°C. The Wheatstone bridge used is shown in Fig. 3. Details of the bridge and a discussion of the bridge circuits are given in the appendix.

Passage of current through the thermistor will cause self-heating, the magnitude of which is dependent on the current, the surrounding medium and the thermal conductivity between thermistor and surroundings. We have used thermistor currents between 0.06 and 0.27 mA, in which cases the deviations from Ohm's law for the thermistor were less than 0.1 %, *i.e.* the amount of self-heating is very small.

The unbalance voltage of the bridge was amplified by using a FLUKE 845 AB microvoltmeter/nulldetector. The amplified voltage was recorded by a Moseley 680 recorder.

Experimental methods. The calorimeter and the various tubings were filled in the following way: The calorimeter was removed from the thermostat and external piston burettes were connected to the glass tubes with the three-way stop-cocks. The tubes (8) and (9) were filled with titrant and solvent, respectively, the stop-cocks were closed and the piston burettes removed. The calorimeter was assembled and put back into the thermostat bath when the inner vessel had been filled with solution, usually 100 cm^3. The external piston burettes were again connected and the space up to the stop-cocks was filled with solution. The calorimeter was ready for operation after thermal equilibrium had been attained.

The total volume of the gas phase in the calorimter is approximately 4 cm^3 as compared to 100 cm^3 in some of the calorimeters previously used.[2] The small volume of the gas phase will minimize heat effects caused by changes of the vapour pressure in the calorimeter.

Addition of titrant was made at a constant rate, usually 1 $cm^3 \cdot min^{-1}$ during the main period. The heat input during the electrical calibrations was made in such a way that the resistance *vs.* time curves followed those of the reactions as closely as possible. The heat changes during the reactions were evaluated by using the usual method with calibration constants.

The volume after each addition of titrant was kept constant and equal to 100 cm^3 by removal of solution from the calorimeter by means of the tube (8) before each experimental determination.

TESTING OF THE CALORIMETER

The thermal leakage constant, K, is an important characteristic of a calorimeter and by determination of K at various times after addition or removal of heat from the system the time of equilibration of the system can be determined.[1] Fig. 2 is a graph of K *vs.* time and shows that the time for equilibration is equal to 4 and 9 min, respectively, after heating or cooling of approximately 100 J. Gerding *et al.*[2] also observed that the time to attain thermal equilibrium was slower after cooling than after heating. The values of K are given in Table 1 and are of the same magnitude as the values found in calorimeters with low-pressure mantles.[1] The rate of temperature change caused by stirring, was constant and equal to 4.2×10^{-4} $K \cdot min^{-1}$.

Reproducibility of the system. The reproducibility of the system was determined by several series of electrical calibrations, where at most 12 J were added to the calorimeter filled with 100.24 cm^3 of water. Calibration constants were then calculated and the results are given in Table 1. An average of thirteen calibrations were made at each temperature and the different columns of the table contain the mean values of ε, the largest deviation,

Table 1. The thermal leakage constant K, and the calibration constants ε, at different temperatures. The largest deviation δ, from the mean, the standard deviation σ, of the individual calibrations and the standard deviation σ_M of the mean are also given.

t °C	$K \times 10^3$ min^{-1}	ε J·ohm^{-1}	δ J·ohm^{-1}	σ J·ohm^{-1}	σ_M J·ohm^{-1}
5.00	4.50	0.8753	0.0013	0.0008	0.0004
20.00	—	1.8159	0.0029	0.0021	0.0008
25.00	4.80	2.2472	0.0033	0.0025	0.0008
35.00	5.05	3.4673	0.0067	0.0050	0.0013
50.00	5.50	6.3936	0.0067	0.0038	0.0013

δ, of a calibration from this mean, the standard deviation of each calibration, σ, and the standard deviation of the mean, σ_M. The standard deviations σ are 0.05–0.15 % and are a measure of the reproducibility of the system. This reproducibility is satisfactory for our purpose.

Determination of the accuracy of the system. The accuracy of the calorimeter was checked at 25°C by determination of the enthalpy changes for three different standard reactions: dilution of hydrochloric acid, reaction of hydrochloric acid with excess potassium hydroxide, and the reaction of tris(hydroxymethyl)aminomethane, THAM, with hydrochloric acid.

Chemicals used, experimental. All chemicals used were of reagent grade. The hydrochloric acid and potassium hydroxide were standardised against thallium(I) carbonate and potassium biphthalate, respectively. The THAM sample was obtained through the courtesy of Dr. Wadsö at the Thermochemical Laboratory, Lund. The hydrochloric acid used for the heats of dilution measurements was 2.006 M. The concentrations of hydrochloric acid and potassium hydroxide used for determination of the heat of ionization of water were 0.1110 M and 9.889×10^{-3} M, respectively. The experiments were carried out by adding the acid to a solution with excess of hydroxide. In this way the carbonate concentration of the solution was kept constant. The THAM buffer used had the composition 0.02000 M THAM, 0.01000 M $THAMH^+$, 0.01000 M Cl^-, *i.e.* an ionic strength equal to 0.0100 M. 0.1001 M hydrochloric acid was used in the titrations. By measuring the hydrogen ion concentration it was possible to correct the measured heat changes for the heat of neutralization of hydroxide ions (*cf.* p. 1073). All alkaline solutions were carefully protected from contamination with carbon dioxide. All experiments were performed as titrations with the calorimeter initially charged with 100.24 cm^3 of solution.

RESULTS

Heats of dilution of hydrochloric acid. The enthalpy changes refer to the process

$$HCl,26.45\ H_2O + (n - 26.45)H_2O \longrightarrow HCl,nH_2O$$

where the values of n are 468.6, 696.5, and 1380.1. Four different series with three successive additions of hydrochloric acid in each series were made. The results are given in Table 2 and a comparison with the SVCTP [4] values is given in Table 3. The difference between the two sets of values is within the error obtained in the graphical evaluation of the SVCTP data.

Table 2. The observed heats of dilution of 2.006 M hydrochloric acid at 25.00°C. n_{HCl} is the number of moles of hydrochloric acid added at each point in the titration. n is the ratio between the number of moles of water and hydrochloric acid.

$n_{HCl} \times 10^3$ mol	n	Q J	$-\Delta H$ J·mol^{-1}	Q J	$-\Delta H$ J·mol^{-1}
4.012	1380.1	9.4381	2353	9.4201	2348
4.012	696.5	8.3595	2217	8.3821	2218
4.012	468.6	7.7302	2119	7.7302	2119
4.012	1380.1	9.4113	2346	9.4180	2348
4.012	696.5	8.3662	2214	8.3842	2218
4.012	468.6	7.7256	2116	7.7302	2119

Table 3. The heats of dilution of hydrochloric acid with their estimated standard deviations at 25.00°C. The last column gives the corresponding data calculated from SVCTP.[4]

n	$-\Delta H$ J·mol^{-1}	$-\Delta H$calc J·mol^{-1}
1380.1	2349 ± 2	2326
696.5	2217 ± 1	2205
468.6	2118 ± 1	2105

Table 4. The heats of neutralization of aqueous hydrochloric acid with aqueous potassium hydroxide and the heat of protonation of THAM at 25°C. Three different series of titrations have been made for the first process and two for the second.

Heat of neutralization			Heat of protonation			
$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H_w^\infty$ kJ·mol^{-1}	$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H$ kJ·mol^{-1}	$-\Delta H_A$ kJ·mol^{-1}
0.2220	12.546	55.86	0.2002	9.5955	47.928	47.47
0.2220	12.534	55.84	0.2002	9.5865	47.903	47.44
0.2220	12.557	55.86	0.2002	9.5730	47.873	47.41
			0.2002	9.6045	47.898	47.44
0.2220	12.546	55.86				
0.2220	12.501	55.76	0.2002	9.5910	47.903	47.44
0.2220	12.548	55.80	0.2002	9.5932	47.911	47.45
			0.2002	9.5977	47.919	47.46
0.2220	12.544	55.86	0.2002	9.5483	47.861	47.40
0.2220	12.559	55.89				
0.2220	12.512	55.84				

Enthalpy of neutralization. Experimental results from three series of titrations are given in Table 4, where the enthalpy values in the last column refer to infinite dilution. The various heats of dilution were obtained from

SVCTP.[4,5] The average value of the heat of ionization of water ΔH_w^∞, equal to 55.84 ± 0.01 kJ·mol^{-1} is in good agreement with the value 55.81 kJ·mol^{-1} given by Vanderzee and Swanson.[6] The error is given as the standard deviation of the mean. If the uncertainty in the hydrochloric acid concentration is taken into account the accuracy of the ionization enthalpy is equal to 55.84 ± 0.05 kJ·mol^{-1}.

Enthalpy of protonation of THAM. The experimental enthalpies of reaction are given in Table 4. All the ΔH-values have been corrected for the heat of neutralization of the hydroxide ions in the alkaline buffer solutions. The corrections were small, at most 10 J. Enthalpy values for the process

$$RNH_2(aq,\ I = 0.01 - 0.02\ M) + HCl(aq) \longrightarrow RNH_4Cl(aq;\ I = 0.01 - 0.02\ M)$$

are given in column six of this table. We have assumed that the heat of dilution of hydrochloric acid is the same in water and in the dilute buffer solution. By calculation of the heats of dilution for the process

$$HCl,550\ H_2O + 27020\ H_2O \longrightarrow HCl,27570\ H_2O$$

from SVCTP [4] we have obtained the enthalpy changes for the process

$$RNH_2(aq,\ I = 0.01 - 0.02\ M) + HCl,27570\ H_2O \longrightarrow RNH_4Cl(aq,\ I = 0.01 - 0.02\ M)$$

These enthalpy values are given in the last column of Table 4. The protonation enthalpy of THAM and its corresponding standard deviation was -47.44 ± 0.01 kJ·mol^{-1}. If the uncertainty in the hydrochloric acid concentration is taken into account, the accuracy of the enthalpy value is equal to ± 0.05 kJ·mol^{-1}.

Öjelund and Wadsö [7] have recently obtained a value of -47.48 ± 0.03 kJ·mol^{-1} for the protonation enthalpy of THAM. The two values are in fair agreement, but it must be remarked that they do not refer to exactly the same process as Öjelund and Wadsö have used solution with a higher ionic strength, approx. 0.07 M.

Conclusions. Both the precision and the accuracy of the calorimeter are satisfactory. The estimated error in the measured enthalpy values is 0.1 – 0.2 % and the largest error, at most 0.1 %, is caused by the uncertainty of the concentration of the hydrochloric acid used.

DETERMINATION OF THE ENTHALPY OF IONIZATION OF WATER, AND THE ENTHALPY OF PROTONATION OF THAM AT 5, 20, 35, and 50°C.

The enthalpy of ionization of water as a function of temperature has been studied by several authors. Most investigators have used emf methods [8,9] and only a few calorimetric determinations have been made (see Ref. 6 for a complete bibliography). Ackermann [10] has made a determination of the partial molar heat capacities of dilute solutions of sodium chloride, sodium hydroxide and hydrochloric acid, and from these data values of $\Delta C_{P,w}^\infty$ for the ionization process can be calculated. This information and an experimental value of the enthalpy of ionization at one temperature, say 25°C, makes it possible to calculate ΔH_w^∞ as a function of temperature.

Table 5. The heats of neutralization of aqueous hydrochloric acid with aqueous sodium hydroxide at the temperatures 5.00, 20.00, 35.00, and 50.00°C.

Temp.→	5.00°C			20.00°C			35.00°C			50.00°C		
Series No.	$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H_w^\infty$ kJ·mol^{-1}	$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H_w^\infty$ kJ·mol^{-1}	$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H_w^\infty$ kJ·mol^{-1}	$n_{HCl} \times 10^3$ mol	Q J	$-\Delta H_w^\infty$ kJ·mol^{-1}
1	0.1665	10.225	61.20	0.2220	12.765	56.96	0.2220	12.055	53.53	0.1665	8.5928	50.65
	0.1665	10.198	61.13	0.2220	12.763	56.96	0.2220	12.059	53.54	0.1665	8.5804	50.61
	0.1665	10.203	61.12				0.2220	12.066	53.55	0.1665	8.5929	50.62
2	0.1665	10.221	61.18	0.2220	12.785	57.06	0.2220	12.059	53.55	0.1665	8.6051	50.72
	0.1665	10.208	61.14	0.2220	12.812	57.11	0.2220	12.114	53.68	0.1665	8.5737	50.63
	0.1665	10.236	61.19				0.2220	12.045	53.61	0.1665	8.5992	50.65
3	0.1665	10.234	61.26	0.2220	12.781	57.04	0.2220	12.062	53.56	0.1665	8.5992	50.68
	0.1665	10.229	61.24	0.2220	12.811	57.10	0.2220	12.055	53.55	0.1665	8.6225	50.76
										0.1665	8.5992	50.73
4	0.1665	10.207	61.10	0.2220	12.770	56.99	0.2220	12.079	53.64	0.1665	8.5737	50.53
	0.1665	10.241	61.20	0.2220	12.774	57.00				0.1665	8.5879	50.57
5	0.1665	10.217	61.16									
	0.1665	10.214	61.15									

Vasil'ev and Lobanov [11] have made a calorimetric determination of the enthalpy of ionization of water at several temperatures between 0 and 70°C. Their results agree better with Harned's values than with those of Ackermann. This is surprising because of the significant discrepancy which exists between Harned's electrometric and other authors' calorimetric values of the standard enthalpy of ionization of water.[6]

In order to check the result of Vasil'ev *et al.* we have made a calorimetric determination of the enthalpy of ionization of water by determining the heat of neutralization of a strong acid, hydrochloric acid, with a strong base, sodium hydroxide, in dilute solution, followed by a correction to infinite dilution.

The enthalpy of protonation of THAM has also been studied by several authors using both emf [12,13] and calorimetric methods.[e.g.7] Calorimetric investigations have been made at only one temperature, 25°C, while the emf studies have been made over the temperature range 0 – 60°C. The enthalpy of protonation values at 25°C obtained by the two methods are in good agreement. Information on the temperature dependence of the enthalpy of protonation has been obtained only from emf-data, which means that the $\Delta C_{P,A}$ data are rather uncertain.[14] We have made this calorimetric determination of the enthalpy of protonation of THAM at several different temperatures in order to get more accurate data of this type, data which then can be compared with those obtained by emf-methods.

EXPERIMENTAL

Chemicals used, calorimetric procedure. 0.1110 M hydrochloric acid and 9.966×10^{-3} M sodium hydroxide solutions were standardized as described before. The THAM buffer was the same as used before. All titrations were made as described before, with three or four additions of titrant in each series. The various heats of dilution at the different temperatures were obtained from the corresponding heats at 25°C and Ackermann's heat capacity data.[10] Values of the partial molar heat capacity $\bar{C}_p$ at the various temperatures and concentrations were obtained from plots of the apparent molar heat capacity *vs.* $\sqrt{m}$, where m is the molality of the electrolyte. Values of $\Delta\bar{C}_p$ for the various dilution processes were then calculated at each temperature and from these values the following functions for the various heats of dilution were obtained.

Dilution of the hydrochloric acid used for determinations of ionization enthalpies

$$\Delta H_{\mathrm{HCl}}/\mathrm{J\cdot mol^{-1}} = -586 - \int_{298.2}^{T} (65.39 - 0.1676\,T)\mathrm{d}T \qquad (1)$$

Dilution of sodium hydroxide solution

$$\Delta H_{\mathrm{NaOH}}/\mathrm{J\cdot mol^{-1}} = -197 - \int_{298.2}^{T} (794.3 - 5.008\,T + 7.950\cdot 10^{-3}\,T^2)\mathrm{d}T \qquad (2)$$

Dilution of sodium chloride solution

$$\Delta H_{\mathrm{NaCl}}/\mathrm{J\cdot mol^{-1}} = -163 - \int_{298.2}^{T} (247.2 - 1.525\,T + 2.407\,T^2)\mathrm{d}T \qquad (3)$$

Table 6. The heat of ionization ΔH_w^∞, and the change in heat capacity $\Delta C_{P,w}^\infty$ for ionization of water in the temperature range 5—50°C. Values of ΔH_w^∞ and $\Delta C_{P,w}^\infty$ obtained from eqns. (5) and (7) and from the literature are also included.

T	ΔH_{exp}^∞	ΔH_w^∞	$\Delta C_{P,w}^\infty$	ΔH_w^∞	$\Delta C_{P,w}^\infty$	ΔH_w^∞
K	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
		rel. 5	rel. 6	Ref. 10	Ref. 10	Ref. 11
278.15	61.17±0.01	61.17	299	61.10	294	
283.15		59.72	282	59.70	278	59.16
288.15		58.34	266	58.35	262	
293.15	57.03±0.02	57.04	250	57.05	248	
298.15	55.84±0.01	55.82	237	55.84	235	56.40
303.15		54.67	224	54.73	225	
308.15	53.58±0.02	53.58	210	53.60	214	
313.15		52.55	199	52.58	206	53.60
318.15		51.58	189	51.57	200	
323.15	50.64±0.02	50.64	179	50.55	189	

Dilution of hydrochloric acid used for determinations of the enthalpies of protonation of THAM

$$\Delta H_{HCl}/\text{J·mol}^{-1} = -464 - \int_{298.2}^{T} (64.02 - 0.1765\,T)\mathrm{d}T \qquad (4)$$

Table 7. The heats of protonation of THAM at

Temp. →		5.00°C				20.00°C		
Series No.	$n_{HCl}\times 10^3$ mol	Q J	$-\Delta H$ kJ·mol^{-1}	$-\Delta H_A$ kJ·mol^{-1}	$n_{HCl}\times 10^3$ mol	Q J	$-\Delta H$ kJ·mol^{-1}	$-\Delta H_A$ kJ·mol^{-1}
	0.15015	7.4135	49.371	49.17	0.20020	9.6582	48.242	47.84
1	0.15015	7.3926	49.300	49.10	0.20020	9.6674	48.262	47.86
	0.15015	7.4022	49.300	49.10	0.20020	9.6582	48.258	47.85
	0.15015	7.4085	49.313	49.11	0.20020	9.6419	48.233	47.83
	0.15015	7.4110	49.354	49.16	0.20020	9.6548	48.225	47.82
2	0.15015	7.4110	49.354	49.16	0.20020	9.6766	48.279	47.88
	0.15015	7.4181	49.371	49.17	0.20020	9.6603	48.271	47.87
	0.15015	7.3926	49.338	49.14	0.20020	9.6749	48.283	47.88
	0.15015	7.4118	49.359	49.16	0.20020	9.6619	48.258	47.85
3	0.15015	7.4164	49.375	49.18	0.20020	9.6548	48.242	47.84
	0.15015	7.3909	49.321	49.12	0.20020	9.6803	48.279	47.88
	0.15015	7.4269	49.359	49.16				
	0.15015	7.4118	49.359	49.16				
4	0.15015	7.4198	49.388	49.19				
	0.15015	7.3894	49.325	49.13				
	0.15015	7.4344	49.371	49.17				

RESULTS

Enthalpy of ionization of water. The experimental enthalpies of neutralization and the corresponding values at infinite dilution are given in Table 5. Table 6 contains the various average values with their corresponding standard deviations. By a least-squares fit the enthalpy values of Table 6 were fitted to the following function of the temperature

$$\Delta H_w^\infty/\mathrm{J\cdot mol^{-1}} = 4.16578\times10^5 - 2.74449\times10^3\ T/\mathrm{K} + 7.031568\ T^2/\mathrm{K^2} - 6.321501\times10^{-3}\ T^3/\mathrm{K^3} \quad (5)$$

Derivation of the preceding eqn. will give $\Delta C_{P,w}^\infty$ as the following function of temperature

$$\Delta C_{P,w}^\infty/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -2744 + 14.063\ T/\mathrm{K} - 1.896\times10^{-2}\ T^2/\mathrm{K^2} \quad (6)$$

Experimental ionization enthalpies obtained by other authors and corresponding values calculated by using Ackermann's heat capacity data are also included in Table 6. A reference value of ΔH_w^∞ at 25°C equal to 55.84 kJ·mol^{-1} was used in the latter calculation. Our results agree well with Ackermann's but not with those of the Russian authors. It may be argued that the results of this investigation are not independent of Ackermann's as we have used his heat capacity values in making the corrections to infinite dilution. However, the heats of dilution are so much smaller than the heats of reaction that the correction is of negligible influence for the comparison.

the temperatures 5.00, 20.00, 35.00, and 50.00°C.

35.00°C				50.00°C			
$n_{HCl}\times10^3$ mol	Q J	$-\Delta H$ kJ·mol^{-1}	$-\Delta H_A$ kJ·mol^{-1}	$n_{HCl}\times10^3$ mol	Q J	$-\Delta H$ kJ·mol^{-1}	$-\Delta H_A$ kJ·mol^{-1}
0.20020	9.4795	47.346	46.78	0.15015	7.0135	46.710	46.02
0.20020	9.4619	47.304	46.74	0.15015	7.0072	46.689	46.00
0.20020	9.4724	47.308	46.74	0.15015	7.0010	46.668	45.98
0.20020	9.4862	47.329	46.76	0.15015	6.9943	46.647	45.96
0.20020	9.4890	47.401	46.83	0.15015	7.0328	46.840	46.15
0.20020	9.5105	47.455	46.89	0.15015	7.0135	46.777	46.08
0.20020	9.4862	47.430	46.86	0.15015	6.9880	46.698	46.01
0.20020	9.4900	47.421	46.85	0.15015	7.0457	46.756	46.06
0.20020	9.4657	47.279	46.71	0.15015	7.0135	46.710	46.02
0.20020	9.5209	47.417	46.85	0.15015	7.0010	46.668	45.98
0.20020	9.4795	47.396	46.83	0.15015	7.0583	46.781	46.09
0.20020	9.4829	47.388	46.82				

The results of the present investigation have thus given a satisfactory confirmation Ackermann's $\bar{C}_P$ values.

Enthalpy of protonation of THAM. The experimental enthalpies of protonation of THAM are given in Table 7, where the last column at each temperature contains the enthalpies of protonation corrected for the heat of dilution of hydrochloric acid (*vide* p. 1073). The protonation enthalpies and their standard deviations are given in Table 8 and these values were fitted by a least-squares method to the following function of temperature

$$\Delta H_A/\mathrm{J\cdot mol^{-1}} = -8.9290\times10^4 + 96.340\ T/\mathrm{K} + 0.5209\ T^2/\mathrm{K^2} - 1.2526\times 10^{-3}\ T^3/\mathrm{K^3} \quad (7)$$

The corresponding expression for the change in heat capacity, $\Delta C_{P,A}$, is

$$\Delta C_{P,A}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 96.3 + 1.0418\ T/\mathrm{K} - 3.7578\times10^{-3}\ T^2/\mathrm{K^2} \quad (8)$$

The values of ΔH_A and $\Delta C_{P,A}$ obtained from the emf data of Bates *et al.*[12] and Datta *et al.* [13] are compared with our results in Table 8. The ΔH_A values

Table 8. The change in enthalpy $-\Delta H_A$ and heat capacity $\Delta C_{P,A}$ for the protonation of THAM. A comparison is made between these figures and those obtained from eqns. (7) and (8) and from literature data.

T	$-\Delta H_A$	$-\Delta H_A$	$\Delta C_{P,A}$	$-\Delta H_A$	$\Delta C_{P,A}$	$-\Delta H_A$	$\Delta C_{P,A}$
K	kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
		rel. 7	rel. 8	Ref. 12	Ref. 12	Ref. 13	Ref. 13
278.15	49.15±0.01	49.15	95.4	48.82	59	50.01	166.9
283.15		48.68	90.0	48.53	60		
288.15		48.25	84.5	48.22	61	48.52	130.6
293.15	47.85±0.01	47.84	78.8	47.91	62		
298.15	47.44±0.01	47.46	72.9	47.60	64	47.40	91.4
303.15		47.11	66.8	47.27	65		
308.15	46.81±0.02	46.79	60.5	46.95	66	46.70	49.2
313.15		46.51	54.1	46.62	67		
318.15		46.25	47.4	46.28	68	46.43	4.1
323.15	46.03±0.02	46.03	40.6	45.94	69		
328.15						46.63	−44.0

obtained by the two methods are in fairly good agreement while the values of $\Delta C_{P,A}$ differ considerably. This is not surprising because of the sensitivity of the second temperature derivative of ΔG° to small experimental errors.[14] In view of this we feel that the present calorimetric data give the more accurate description of the temperature variation of the heat of ionization of THAM.

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APPENDIX

The bridge used in the temperature measurements is shown in Fig. 3. The unbalance voltage from the bridge is amplified by the zero instrument and is then recorded. In

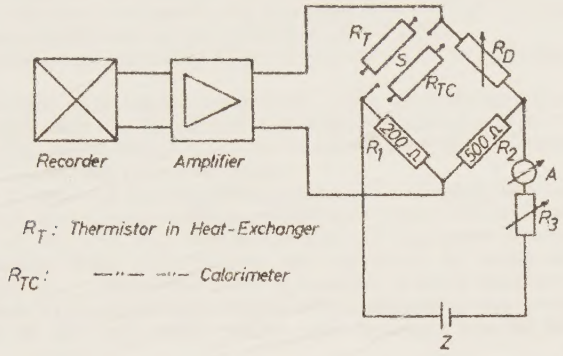

Fig. 3. The bridge and recording system used. The bridge is made of the parts described on p. 1070. S is a switch used to interchange the calorimeter thermistor, R_T, and the heat-exchanger thermistor R_{TC} in the bridge circuit.

this way a continuous record of resistance *vs.* time is obtained. The unbalance voltage is directly proportional to the thermistor current, which in turn is limited by the amount of self-heating that can be tolerated. The bridge and the zero instrument are chosen so as to give the largest possible signal with respect to the noise in the system. A discussion of the bridge and amplifier circuits is facilitated if they are replaced by their equivalent Thevenin circuits according to Fig. 4. The effective unbalance reading as read on the

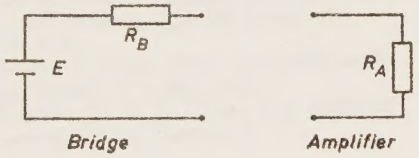

Fig. 4. Thevenin equivalent circuits of the bridge and amplifier.

amplifier input is equal to $E \cdot R_A/(R_A+R_B)$. Both E and R_B depend on the ratios of the bridge arms.

$$E = I_T \cdot \Delta R_T \frac{R_D}{R_T+R_D} \tag{1}$$

$$R_B = R_T \cdot \frac{R_D}{R_T+R_D} \cdot \left(1+\frac{R_1}{R_T}\right) \tag{2}$$

ΔR_T is the difference between the thermistor resistance and the bridge reading ("the unbalance resistance").

In the bridge used R_B is of little concern, since $R_A \gg R_B$. Generally, R_B should be kept small by making R_1/R_T small. By using an unsymmetrical bridge we have increased the unbalance voltage, E, to the value $0.715 \cdot I_T \cdot \Delta R_T$ as compared to $0.5 \cdot I_T \cdot \Delta R_T$ in the symmetrical bridge.

The accuracy of the resistance measurements is approximately $\pm 4 \times 10^{-4}\Omega$ (± 0.5 ppm), corresponding to a temperature accuracy of $\pm 2 \times 10^{-6}$°C. It is essential to reduce various sources of noise in order to obtain this accuracy. The following points are the most important: The temperature control of the surroundings is important in order to reduce resistance fluctuations in the bridge resistors (temperature coefficient 20 ppm/K).

The insulation of the thermistor circuit must be good. The leakage conductance in the thermistor connections must vary less than $2.5 \times 10^{-10}\Omega^{-1}$ in order to obtain an accuracy of $10^{-3}\Omega$. This corresponds to an insulation of $4 \times 10^{9}\Omega$.

Contact resistance variations must be less than $10^{-3}\Omega$. Thermopotentials must be less than 0.1 μV.

Hum (voltages with mains frequency) must be reduced below 100 μV by screening out electric and magnetic fields and avoiding ground currents.

With careful construction, the above mentioned claims were met and the amplifier became the dominating source of noise.

The noise present on the amplifier input can be divided into two parts, a noise voltage in series with E, and a noise voltage caused by a noise current flowing through the parallel combination of R_A and R_B. The latter part of the noise is reduced by keeping R_B as small as possible. Fast disturbances are supressed by using an amplifier with a low limiting frequency, 1 Hz in this case. A recorder is more sensitive to noise and hum than a galvanometer. It is nevertheless more advantageous to use a recorder than a galvanometer because of the ease with which time averages can be determined in the former case.

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